

# ROMP of norbornene catalysed by Grubbs functionalized carbon nanotubes

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## ABSTRACT

The synthesis of polynorbornene by ring opening metathesis polymerization (ROMP) in the presence of 1<sup>st</sup> generation Grubbs catalyst-functionalized nanotubes, is reported.

A characterization of the 2<sup>nd</sup> generation Grubbs catalyst-functionalized nanotubes was performed by TGA (Thermogravimetric Analysis) on-line connected with a quadrupole-mass spectrometer, in order to quantify the amount of catalyst grafted to the nanotube surface.

The activities of the catalyst-functionalized nanotubes in ROMP of 2-norbornene were compared with those of pure 2<sup>nd</sup> generation Grubbs catalysts.

**Keywords:** ROMP, Grubbs catalyst, carbon nanotubes, norbornene

## 1 INTRODUCTION

Since their discovery in 1991 carbon nanotubes have emerged, for their unique structural and electronic properties, as one of the leading materials for a wide array of potential nanotechnological applications. Their high strength and Young's modulus make them attractive as fillers in polymer nanocomposites. Nevertheless, their aggregative properties, caused by strong van der Waals forces, prevent a good dispersion in the polymeric matrix, which is a prerequisite for an optimized interfacial stress transfer with the polymer. Indeed, the synthesis of homogeneous polymeric materials containing carbon nanotubes (CNTs), able to combine the mechanical strength and electronic conductivity of carbon nanotubes with the solubility and processability of polymers, still represents a challenge.

Herein, a synthetic strategy [1] has been adopted to functionalize multi-walled carbon nanotubes (MWCNT) with 2<sup>nd</sup> generation (G2) Grubbs catalyst [2], and their activity as initiators for ROMP of 2-norbornene has been tested and compared with the activity of bare G2. The catalyst-functionalized nanotubes have been characterized by TGA, in order to quantify the amount of catalyst grafted to the nanotube surface. To the best of our knowledge, this is the first time that the activity of catalyst-functionalized nanotubes, as polymerization initiators, has been estimated.

The obtained polymer-functionalized nanotubes have been characterized by scanning electron microscopy (SEM) images.

## 2 EXPERIMENTAL

### 2.1 Materials and methods

#### *Carbon nanotubes*

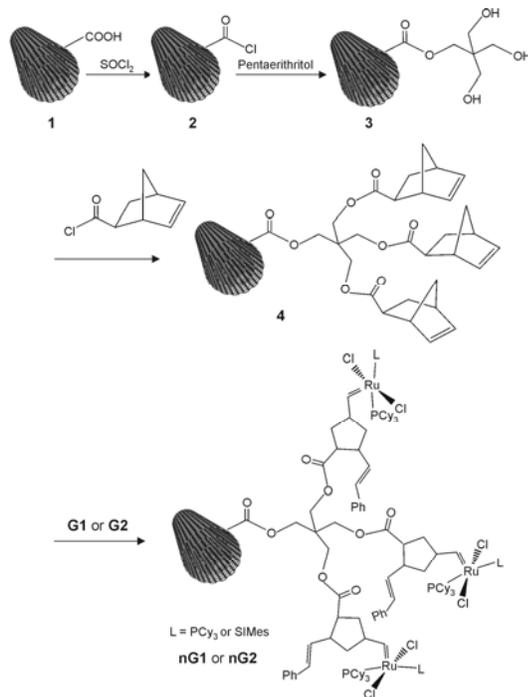
Carbon nanotubes have been prepared by catalytic ethylene chemical vapor deposition (CVD) [3-4] on Co/Fe modified Al<sub>2</sub>O<sub>3</sub> powder. Co, Fe catalysts (2.5 wt% of each metal) were prepared by dry impregnation with a cobalt acetate and iron acetate solution of gibbsite. The catalyst was dried at 393 K for 720 min, and preheated before synthesis at 70 K/min up to 973 K under N<sub>2</sub> flow. For the CNT synthesis a mixture of ethylene in nitrogen was fed to a continuous flow microreactor at 973 K, with a runtime of 30 min. Gases flow rate, controlled by calibrated Brooks mass flow controllers, and catalyst mass were 120 (stp)cm<sup>3</sup>/min (10% v/v of C<sub>2</sub>H<sub>4</sub> in N<sub>2</sub>) and 400 mg respectively. The syntheses were performed in the experimental plant equipped with on-line ABB analyzers that permit the monitoring of C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub> concentrations in the effluent stream on line during the reaction. The synthesis was very effective, yielding more than 97% conversion of the injected carbon and about 100% selectivity to MWNT. To remove catalyst the synthesized samples were treated with HF (46% aqueous solution), and the solid residue was washed with distilled water, centrifuged and finally dried at 353 K for 12 h, resulting in high purity (> 97%) MWNT.

MWNTs have been characterized by Transmission (TEM) and Scanning (SEM) Electron Microscopy (TEM) images were performed using a Philips CM30T electron microscopy with a LaB<sub>6</sub> filament as source of electrons operated at 300 kV.

SEM pictures were obtained with a LEO 420 microscope.

For the -COOH functionalization, MWNTs were treated with H<sub>2</sub>SO<sub>4</sub>98% / HNO<sub>3</sub>65%, 3:1 mixture (8 mg/ml) at 55°C in a low power sonic bath. After 20 min the suspension was diluted with distilled water and filtered on a 0.1 Millipore polycarbonate membrane. The solid was

washed with NaOH solution to remove the carbonaceous waste and then with HCl solution to establish carboxylic groups attached to the nanotubes; a thick paper-like material was suspended in H<sub>2</sub>SO<sub>4</sub>98% / H<sub>2</sub>O230% 4:1 mixture, and stirred for 30 min at 70°C (etching treatment) to remove wastes aggregate on the tube walls not completely dissolved during the previous washing of the membrane. The mixture, cooled to room temperature, was washed, filtered and finally dried at 120°C for 12 h.



Scheme 1

The MWCNTs were functionalized by following the procedure reported by Adronov et al. [1]. As sketched in Scheme 1, the carboxylic acid functionalized nanotubes (1) were reacted with thionyl chloride resulting in the corresponding acid chloride (2), and treated, in situ, with pentaerythritol in order to obtain three corresponding primary alcohol functionalities (3). The triol functionalized nanotubes were reacted with the 5-acid chloride 2-norbornene, resulting in norbornene functionalized nanotubes (4). The reaction between the latter and G2, gives a metathesis reaction resulting in the 2<sup>nd</sup> generation Grubbs catalyst functionalized nanotubes, nG2.

nG2 showed to be insoluble in the most common solvents were characterized by TGA.

The total amount of catalyst in nG2 was evaluated by TGA.

ROMP of 2-norbornene was performed in the presence of nG2 and compared with the polymerization in the presence of G2. The results are reported in terms of activity in the following section.

The obtained composites have been characterized by SEM.

## 2.2 Results and discussion

Figure 1 shows a typical SEM picture of the as produced bundle of nanotubes as grown from the catalyst, with a length of about 200 μm. Nanotubes are multiwalled with an external diameter ranging from 9 to 23 nm, while the internal diameter varies from 5 to 8 nm (see Figure 2).

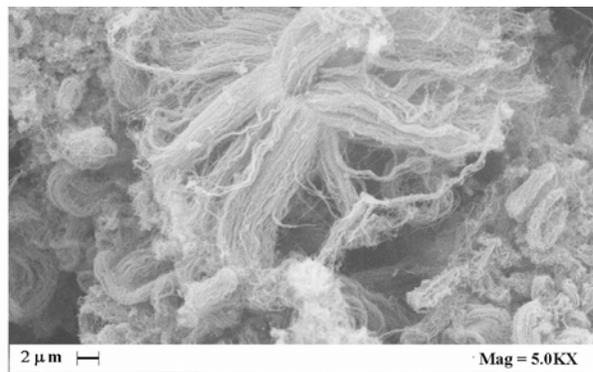


Figure 1: SEM image of as produced MWNT

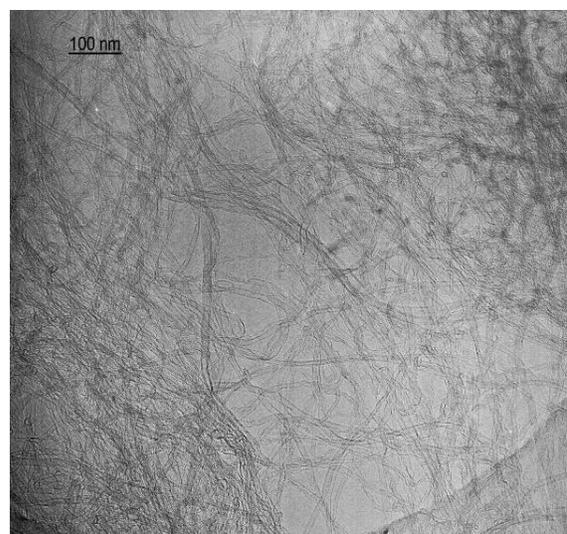


Figure 2: TEM image of as produced MWNT

In Figure 3 the thermogravimetric profiles, obtained in air of G2, nG2 and -COOH functionalized MWNTs (NT), are reported for comparison. At a temperature of 460°C the oxidation of the 79.6 wt.% of G2 is completed, the remaining 20.4 wt% partially oxidized after this temperature and will constitute the TG residue. NT exhibits one peak of weight loss in the range 580-710°C. However, in the thermogravimetric profile of nG2 we can distinguish three distinct weight losses. In particular, from the DTG profiles, we can evaluate three peaks, in the range 180-440°C, 380-590°C, 490-710°C, the first two due to the oxidation of G2, the third one to the combustion of

functionalized CNT, as confirmed by the ion currents fragments, given by mass spectrometer in the same temperature range. The ion currents of G2 and mass fragments of CO<sub>2</sub> by the NT oxidation were acquired by the mass spectrophotometer interfaced with TG balance. So, considering that the first two weight losses (25 wt.% of nG2) are due to G2 and that they constitute the 79.6% of the total catalyst, the amount of G2 in nG2 is equal to 31.4 wt%.

ROMP of 2-norbornene was performed in the presence of nG2 and compared with the polymerization in the presence of G2. All results are reported in Table 1. The reaction conditions for run 1-4 were chosen in order to have low conversions (below 10%) of the monomer and, as a consequence, to consider the monomer concentration constant during the run. Indeed, this allows a fine estimation of the catalyst activities, that were calculated for run 3 and 4. As reported in Table 2, the activity of G2 is slightly lower than that of nG2. Basically, the activity does not change if G2 is grafted to MWCNTs.

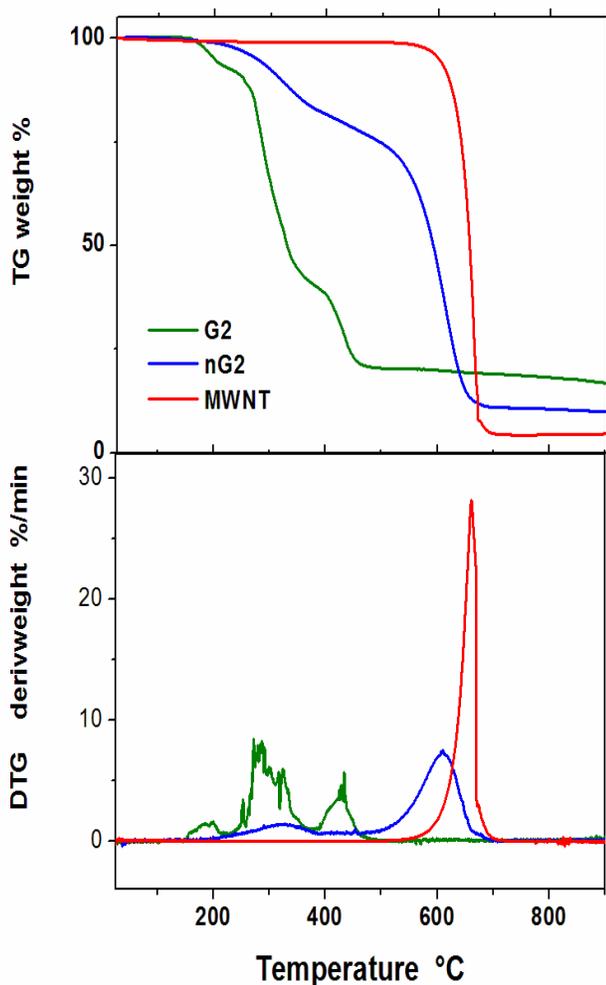


Figure 3: TG-DTG of G2, nG2 and COOH-functionalized MWNT

Table 1: Polymerization of 2-norbornene.

Run	Initiator	Solvent	Activity*
2	<b>G2</b>	CH <sub>2</sub> Cl <sub>2</sub>	2.29*10 <sup>6</sup>
4	<b>nG2</b>	CH <sub>2</sub> Cl <sub>2</sub>	4.38*10 <sup>6</sup>

\*Activity:  $g_{polymer}/[monomer][catalyst]h$ .

In Figure 4 is reported a SEM picture of the polymer obtained by nG2, showing carbon nanotubes completely covered by polymer.

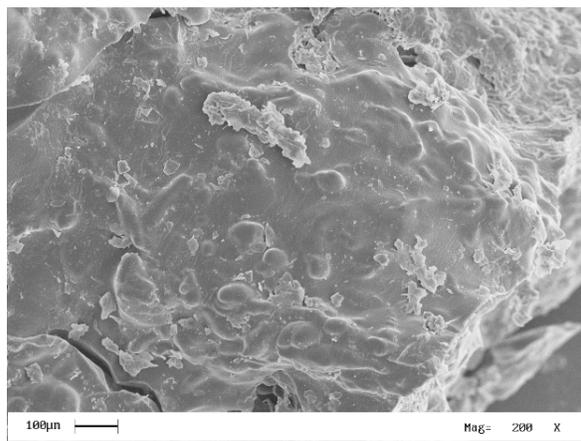


Figure 4: SEM image of the polymer obtained by nG2

### 3 CONCLUSION

The synthesis of polynorbornene by ring opening metathesis polymerization (ROMP) in the presence of 1<sup>st</sup> and 2<sup>nd</sup> generation Grubbs catalyst-functionalized nanotubes, has been obtained.

The amount of catalyst grafted to the nanotube surface has been quantified by TGA on-line connected with a quadrupole-mass spectrometer, for both 1<sup>st</sup> and 2<sup>nd</sup> generation Grubbs catalyst-functionalized nanotubes.

The activities of the catalyst-functionalized nanotubes in ROMP of 2-norbornene were compared with those of pure 1<sup>st</sup> and 2<sup>nd</sup> generation Grubbs catalysts. The activity of G2 are slightly lower than that of nG2, retaining the same order of magnitude.

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